Ionization Rates and Charge Production in Hydrocarbon Fuels

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In fuel air mixtures the electron energy distribution function (EEDF) is dominated by the effects of the nitrogen momentum transfer and inelastic collisions. However the ionization potential of the hydrocarbons, n-octane and n-decane, are about 11.7 eV and 10.2 eV respectively whereas the nitrogen ionization potential is 15.5eV. Therefore the total ionization rate at higher fuel ratios can be dominated by ionization of the fuel. On the other hand in vitiated air, nitric oxide is produced and it has an even lower ionization potential. If NO (ionization potential 9.25 eV) is present in small quantities, it will also be an important source of ionization even though the EEDF is still controlled by nitrogen. The charge transfer rates also lead to ionization of the lowest ionization potential species.

Charged-particle collisions contribute to the ignition process by producing radicals, cracking the fuel molecules, and increasing the gas temperature through heat released from exothermic reactions. This paper presents our studies using Fourier-transform mass spectrometry (FTMS) on the fuel compounds, n-octane and decane and nitromethane. We have measured their electron impact ionization and gas-phase ion-molecule reactions. Calibration using argon allowed absolute ionization cross-sections and charge exchange rates of cracked ions with the parent molecules to be obtained. Ion-molecule reactions proceed much more rapidly than neutral radical-molecule reactions and therefore will be important at sufficient ionization fraction in the breakdown and expansion phases of the spark ignition process. The power into the plasma is given by the product of the voltage (time) and current (time) and it is important to measure accurately the phase between these two parameters in order to quantify the energy input.

In earlier work, the percentage of ionized fragments produced by removing hydrogen without breaking carbon-carbon bonds is found to decrease as the molecular weights of the paraffins increase. Thus our data correlate with the earlier observations that while 84% of the ions formed from ethane do not involve carbon-carbon bond scission, only 0.008% do so from n-octane.[18]

All of the experiments are performed using a modified Fourier-transform mass spectrometer (FTMS) equipped with a cubic ion cyclotron resonance trapping cell (5 cm on a side) and a 2 T

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superconducting magnet.[19] Typically, n-octane (99+%) is mixed with argon (99.999%) with a ratio about 1:1 to a total pressure of ~2 Torr. For the isotope reagent experiments, octane-d_{18} is mixed with octane and argon with a ratio of ~1:1:2. The technique of collision-induced dissociation (CID) in FTMS goes as follows: the ion to be studied is first isolated and then kinetically excited to an energy level in the range from a fraction of an eV to a few hundred eV. This excitation to higher energy typically takes place in a time short compared to the collision time with the neutral background gas. In a subsequent collision with a neutral gas molecule, part of the kinetic energy may be converted to internal energy, which may lead to the dissociation of the reactant ion, yielding smaller fragment ions.
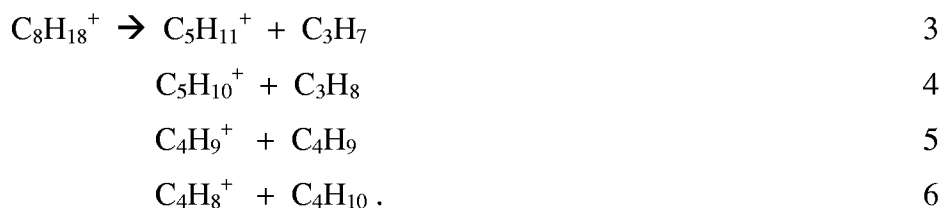
The electron impact ionization of n-octane produces a modest amount of the parent molecular ion and a host of fragment molecular ions ranging from those containing a single carbon atom to those with six carbon atoms. At energies below 16 electron volts, the ionization products are $C_6H_{13}^+$ and $C_6H_{12}^+$, with the neutral partners assumed to be the C_2H_5 radical and the C_2H_6 molecule, respectively. These products are believed to result from the primary decomposition (i.e., decomposition directly from the molecular ion). At higher energies, successive decomposition (i.e., subsequent decomposition from the daughter ions) becomes more important and $C_3H_7^+$ becomes the most abundant ion with the neutral fragments being a complicated mixture of various radicals and small hydrocarbon molecules. The total ionization cross-section as well as partial ionization cross-sections has been measured. The total ionization cross-section rises dramatically near threshold (12 - 20 eV) and levels off at ~ 60 eV with a value of $1.4 \pm 0.2 \times 10^{-15}$ cm^2. This cross-section data can be used in determining the primary electron ionization coefficient,[25] which is one of the key parameters in the breakdown numerical simulation.[13-15] The cross-section data can also be used directly in other aspects of the kinetic model calculation.[12]

All of the fragment ions are formed by the fragmentation of the molecular ion via the C-C bond cleavage and through one of the two paths: (1) primary decomposition or (2) successive decomposition. The fragmentation can be (1) a simple C-C bond cleavage, or (2) accompanied by atom rearrangement.

$$C_8H_{18}^+ \rightarrow C_6H_{13}^+ + C_2H_5 \qquad\qquad 1$$
$$C_6H_{12}^+ + C_2H_6 . \qquad\qquad 2$$

While reaction 1 is a simple C-C bond split process, reaction 2 is via a H-atom rearrangement before or during the C-C bond cleavage. It has been noted that compared to a simple single-bond cleavage, a bond cleavage with rearrangement has relatively small activation energy and frequency

factor.[27] The data for $C_6H_{12}^+$ and $C_6H_{13}^+$ shown in figure 3 exhibit this characteristic: the $C_6H_{12}^+$ cross section has a lower onset energy but then rises relatively slowly, while the $C_6H_{13}^+$ cross section has a higher onset energy but rises faster. The formation of $C_5H_{11}^+$ vs. $C_5H_{10}^+$ and $C_4H_9^+$ vs. $C_4H_8^+$ near their thresholds exhibit similar trends and the following fragmentation processes at low ionizing energies are implied:

$$C_8H_{18}^+ \rightarrow C_5H_{11}^+ + C_3H_7 \qquad\qquad 3$$

$$C_5H_{10}^+ + C_3H_8 \qquad\qquad 4$$

$$C_4H_9^+ + C_4H_9 \qquad\qquad 5$$

$$C_4H_8^+ + C_4H_{10} \, . \qquad\qquad 6$$

The ion population generated from the electron impact ionization relaxes to a stable composition via ion-molecule reactions. In our study it is found that $C_4H_7^+$ and smaller ions undergo reactions with the parent molecule via an alkide-abstraction mechanism, while the larger ions are basically unreactive. The reaction kinetics for some selected reactive ions that have ionization cross sections greater than 10^{-17} cm^2 at 50 eV are studied with the results shown in table 1. The reaction rates for the observed reactions range from 0.32 x 10^{-9} cm^{3}s^{-1} to 2.4 x 10^{-9} cm^{3}s^{-1}, with a general trend of increasing reactivity with the decreasing number of carbon atoms in the reactant ion. The major ionic products from the observed reactions are $C_5H_{11}^+$ and $C_4H_9^+$, with the neutral products to be various hydrocarbon molecules; no radicals is produced in general. Relatively small amounts of $C_3H_7^+$ and $C_3H_5^+$ are also produced from small C_n^+, and these two product ions can undergo secondary reactions with n-octane to finally form $C_5H_{11}^+$ and $C_4H_9^+$ that are unreactive with n-octane. The reactions in table 1 proceed through one or more of the following mechanisms that have been proposed in the literature for ion-molecule reactions involving paraffin molecules: oxidative-insertion-complex formation, charge-transfer, $H^{+,0,-}$-abstraction, or alkide (R^-)-abstraction. To probe the reaction mechanisms, different ions from n-octane are isolated and allowed to react individually with n-C_8H_{18} and, in another separate experiment, with a mixture of n-C_8H_{18} and n-C_8D_{18} (1:1 ratio). No isotope exchange between the reactant ion and n-octane has been observed for all of the reactions in table 1. For example, when $C_3H_7^+$ reacts with $[C_8H_{18}, C_8D_{18}]$, only $C_5H_{11}^+$, $C_5D_{11}^+$, $C_4H_9^+$ and $C_4D_9^+$ are detected. No mixed-isotope ions, such as $C_5HD_{10}^+$ or $C_4HD_8^+$, are present. This finding appears to exclude the possibility of an oxidative-insertion-complex formation mechanism and a $H^{+,0}$-abstraction mechanism; with these mechanisms the isotope in the reactant ions should have been more or less retained in the product ions. A charge-transfer mechanism is also unlikely based on the fact that many reactant ions have lower ionization

potentials than the appearance potentials of the product ions by a few eV, which means that the reactions in table 1 would have been rather endothermic if they were via the charge-transfer mechanism. For example, $C_2H_5^+$ reacting with n-octane via charge-transfer to produce $C_5H_{11}^+$ and $C_4H_9^+$ would be endothermic by 3.0 and 2.8 eV, respectively.[30] Therefore, only the hydride- and alkide- abstractions are left as candidates for the possible reaction mechanisms. In our experiments, no M-1 ion from any of the ion-molecule reactions studied has been found. Also, we observed no significant kinetic isotope effect in the isotope reagent experiments. For example, $C_3H_7^+$ reacting with $[C_8H_{18}, C_8D_{18}]$ produces equal amounts of $C_5H_{11}^+$ and $C_5D_{11}^+$, and equal amounts of $C_4H_9^+$ and $C_4D_9^+$; also, when $C_3D_7^+$ is used as the reactant ion, the reaction rate and the product distribution remain the same as those for $C_3H_7^+$. We propose that the alkide-transfer is likely to be involved in the majority of the reactions. In summary, the ion population generated by electron impact ionization and modified by the ion-molecule reactions is dominated by, depending on the electron ionization energy, $C_6H_{13}^+$ and $C_6H_{12}^+$ (low energies) or $C_5H_{11}^+$ and $C_4H_9^+$ (high energies), which are stable toward their parent molecule. One fate of the stable ions is dissociative recombination (DR) with electrons. Mitchell[26] has shown that many hydrocarbon ions recombine with rate constants of the order of 10^{-6} cm^3sec^{-1}. Combination of the concentration ratio of electrons vs. neutral gas molecules in the order of 10^{-6} and the ratio of second-order rates of DR vs. ion-molecule reactions in the order of 10^3 yields the first-order rates of DR lower than the ion-molecule reaction by an order of 10^{-3}. In the case of $C_4H_7^+$ and smaller ions, DR cannot compete against their reaction rates with the parent molecule. However, for the unreactive ion or for the stable final product ions from the ion-molecule reactions, DR is a possible channel for the ions to contribute to the ignition process, generally producing one or more neutral radical species.

The chemistries of ions with increased kinetic energy have also been studied using the CID technique. Each of the different ions is isolated and kinetically excited to a certain energy level, followed by a collision time for the ion to react with n-octane. The CID results are usually presented qualitatively or semi-quantitatively, because with today's FTMS techniques reliable CID reaction rates at well-defined energies are difficult to acquire even for reactant ions that are initially thermalized. Here we report only the products from the kinetically excited ion reactions. At these elevated energies ions can potentially undergo all of the possible reactions including charge-transfer and H^- or R^- abstraction, as well as CID. We find that essentially only the CID processes are involved. For example, when $C_5H_{11}^+$ is kinetically excited (here designated as $C_5H_{11}^{+*}$) we find,

$$C_5H_{11}^{+*} + M \rightarrow C_3H_7^+ + C_2H_4 + M,$$

where M represents the neutral collision target. The CID process is distinguished from the other endothermic reactions by the product isotope pattern. When $C_5H_{11}^+$ reacts with a 1:1 mixture of C_8H_{18} and C_8D_{18}, only $C_3H_7^+$ is observed:

$$C_5H_{11}^{+*} + M \rightarrow C_3H_7^+ + C_2H_4 + M \, ,$$
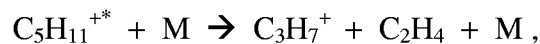
where $M = [C_8H_{18}, C_8D_{18}]$. The amount of product $C_3D_7^+$ is insignificant. To determine if this product selectivity is not due to the kinetic isotope effect, $C_5D_{11}^+$ is used as the reactant ion. Then, essentially only $C_3D_7^+$ is observed:

$$C_5D_{11}^{+*} + M \rightarrow C_3D_7^+ + C_2D_4 + M \, .$$

Clearly, these experimental results indicate that the reaction of $C_5D_{11}^{+*}$ is a CID process. Similar experiments show that CID is also the major endothermic reaction observed for other kinetically excited ions. For the molecular ion $C_8H_{18}^{+*}$, the reaction with $[C_8H_{18}, C_8D_{18}]$ produces $C_5H_{11}^+$, $C_4H_9^+$, $C_3H_7^+$, and relatively small amounts of the corresponding d-isotope ions, which suggests that the CID of $C_8H_{18}^{+*}$ is mixed with other reaction(s). These other reactions are unlikely to be a H⁻ or R⁻ abstraction reaction because all of the C atoms in this $C_8H_{18}^+$ are fully ligated. The charge transfer reaction is most likely the one involved.

The CID product ions, if smaller than $C_4H_7^+$, are observed to undergo the same reactions listed in table 1 for the corresponding ions from the electron impact ionization, although whether the CID product ions have the same structures as the corresponding ions from the electron impact ionization is in question. A study in the 1970's on CID of isomeric octane ions demonstrated that structurally isomeric ions isomerize to a common structure prior to decomposition.[34] On the other hand, another study showed that the alkyl ions from the electron impact ionization on hydrocarbons might be a mixture of structural isomers.[35] We do not see different reaction rates for the isomers when they occur; for all of the reactions in table 1, i.e., no double-exponential decay of the reactant ion has been observed.

From the results presented above we conclude that, if the ion temperature is high enough to drive its "thermal decomposition", there may be a reaction cycle in the n-octane plasma: the reactant ion is reacted away with n-octane, while the product ion decomposes to regenerate the reactant ion, and the reaction goes on.

The ion formation in n-decane is studied and compared with that of n-octane. The total ionization for n-decane is similar to that of n-octane, also increasing sharply from the threshold to ~20 eV. The partial ionization cross sections are different. At high energies, the prevailing product ion is $C_4H_9^+$. At low energies (<14 eV), the electron impact on n-decane produces predominantly

parent ion $C_{10}H_{22}^{+}$, along with minor products through four dissociative channels: $C_7H_{14}^{+} + C_3H_8$, $C_7H_{13}^{+} + C_3H_7$, $C_5H_{11}^{+} + C_5H_{11}$ and $C_4H_9^{+} + C_6H_{13}$. The difference in the low energy ionization behaviors of n-octane and n-decane is important. The ionization of octane produces major products including the C_2H_5 radical, which in turn undergoes collisional dissociation to form C_2H_4 and H atom, --- one of the principal radical branching center in combustion, the ionization of n-decane does not produce neutral radicals as fast as octane. This finding suggests that the role played by the electron impact ionization process in n-decane may not be as important as in n-octane, in the aspect of contribution to the building up the radical concentration.

This series of detailed experiments has produced absolute data for electron impact ionization of n-octane, decane and nitromethane. Some of the important ion molecule reactions that occur between the fragment molecular ions and their parent molecules have also been measured. It appears that under high gas temperature conditions, fragment ions from n-octane can act catalytically to produce multiple free radicals per ion. The details of the measurements agree with earlier qualitative work that found that the probability of carbon-carbon bond splitting was small for those bonds at the ends of the hydrocarbon molecule and increases to a maximum at the third or fourth bonds from the ends. This pattern gives rise to an M-shaped relative fragmentation index.[36]

Usually one may expect that after the electron impact ionization, the relaxation of the ion composition by ion-molecule reactions leads to a stable ion composition; the ion-molecule reactions convert the reactive ions to more stable product ions and at the end all of the ions are unreactive. The present study demonstrates that at slightly elevated energies the reactive ions can be recycled, and reaction chains can be accomplished that repeatedly convert large paraffins into smaller hydrocarbon molecules.

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